

UNCLASSIFIED

AD NUMBER
AD869155
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; APR 1970. Other requests shall be referred to U.S. Army Electronics Command, Attn: AMSEL-KL-PB, Fort Monmouth, NJ 07703-5601.
AUTHORITY
Army Electronics Command ltr dtd 27 Jul 1971

THIS PAGE IS UNCLASSIFIED

AD

AD 869155



Research and Development Technical Report
ECOM- 0143-3

ELECTRODE-ELECTROLYTE INTERACTIONS

MAGNESIUM ANODES : : meta-DINITROBENZENE CATHODES

THIRD SEMI-ANNUAL REPORT

By

A. ADUBIFA

G. SMALDONE

G. STERN

L. WIKSTROM

APRIL, 1970

DISTRIBUTION STATEMENT

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of CG, U.S. Army Electronics Command, Fort Monmouth, N. J.

Attn: AMSEL- KL-PB

ECOM

UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.

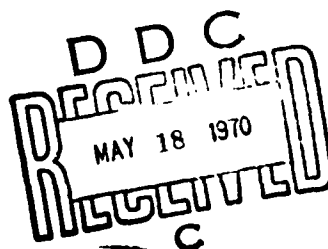
CONTRACT DAAB07-68-C-0143

NEW YORK UNIVERSITY

CHEMICAL ENGINEERING DEPARTMENT

Bronx, N. Y.

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va 22151



23

Electrode - Electrolyte Interactions
Magnesium Anodes: meta-Dinitrobenzene Cathodes

1 January 1969 to 30 June 1969

Report No. 3

Contract No. DAAB07 - 68-C-0143

Prepared by

A. Adubifa

G. Smaldone

G. Stern

L. Wikstrom

NEW YORK UNIVERSITY
DEPARTMENT OF CHEMICAL ENGINEERING
U. S. ARMY ELECTRONICS COMMAND
FORT MONMOUTH, NEW JERSEY

Table of Contents

	<u>Page No.</u>
List of Figures	i
Abstract	1
Purpose	2
Introduction	3
Experimental Procedure	3
Results and Discussion	6
Conclusions	14
Recommendation for Future Research	15
Identification of Key Personnel	16
Bibliography	17
Distribution List	

List of Figures

	<u>Page No.</u>
Figure 1 m-DNB Cathode Assembly	5
Figure 2 Polarization Data	7
Effect of Mg^{++}/Na^{+} Ratio on Mg Dissolution	
-1.80v vs SCE Starting Potential	
Figure 3 Polarization Data	9
Effect of Mg^{++}/Na^{+} Ratio on Mg Dissolution	
-1.70v vs SCE Starting Potential	
Figure 4 Polarization Data	10
Effect of Starting Potential on Mg Dissolution	
2.8M $NaClO_4$ - 0.6M $Mg(ClO_4)_2$	
Figure 5 Polarization Data	11
Effect of $Sr(ClO_4)_2$ Concentration	
Figure 6 Polarization Data	13
Reduction of mDNB in $NaClO_4$ and $Mg(ClO_4)_2$	

Abstract

The electrochemical dissolution of magnesium (AZ-21) and hydrogen evolution reaction on magnesium in $\text{Mg}(\text{ClO}_4)_2$, $\text{Sr}(\text{ClO}_4)_2$, NaClO_4 and $\text{NaClO}_4 - \text{Mg}(\text{ClO}_4)_2$ electrolyte mix have been investigated. The electrochemical reduction of meta-dinitrobenzene in NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$ has also been studied. Polarization data indicate the corrosion current density of the magnesium electrode is much smaller in the NaClO_4 than in the other electrolytes studied. In the $\text{NaClO}_4 - \text{Mg}(\text{ClO}_4)_2$ electrolyte mix the corrosion current density of the magnesium electrode increases as the proportion of $\text{Mg}(\text{ClO}_4)_2$ is increased. In the mixed electrolyte system the magnesium electrode can exhibit two distinctly different corrosion current densities. These corrosion current densities are dependent upon the history of the electrode.

The rate of meta-dinitrobenzene reduction in NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$ was found to be about equal. Even though the reduction rate in the two electrolytes was equal, different reaction products apparently were formed.

Purpose

The purpose of this study is to investigate the electrochemical characteristics of the magnesium anode and the meta-dinitrobenzene cathode in like electrolytes. Much emphasis was paid to the reproducibility of the polarization data.

Introduction

Previously, the initial results of the investigation of the electrochemical dissolution and corrosion of magnesium and the reduction of meta-dinitrobenzene in aqueous electrolyte were reported^(1,2). A review of the pertinent literature was also presented⁽¹⁾. The material presented within this report represents a continuation of the work described earlier⁽¹⁾.

Experimental Procedure

The electrochemical cell, three electrode system employed, and the experimental procedure followed for the investigation of the magnesium electrodes (AZ-21) were described previously⁽¹⁾. Starting potentials of -1.65v, -1.7v, -1.75v, -1.80v, and -1.85v with potential increments of 25 mv were used in this investigation. The electrolytes used are listed in Table I.

TABLE I
ELECTROLYTES INVESTIGATED

2.0M	Mg(ClC ₄) ₂
4.0M	NaClC ₄
3.96M	NaClC ₄ - 0.02M Mg(ClC ₄) ₂
3.60M	NaClC ₄ - 0.2M Mg(ClC ₄) ₂
2.80M	NaClC ₄ - 0.6M Mg(ClC ₄) ₂
0.5M	Sr(ClC ₄) ₂
1.0M	Sr(ClC ₄) ₂
2.0M	Sr(ClC ₄) ₂

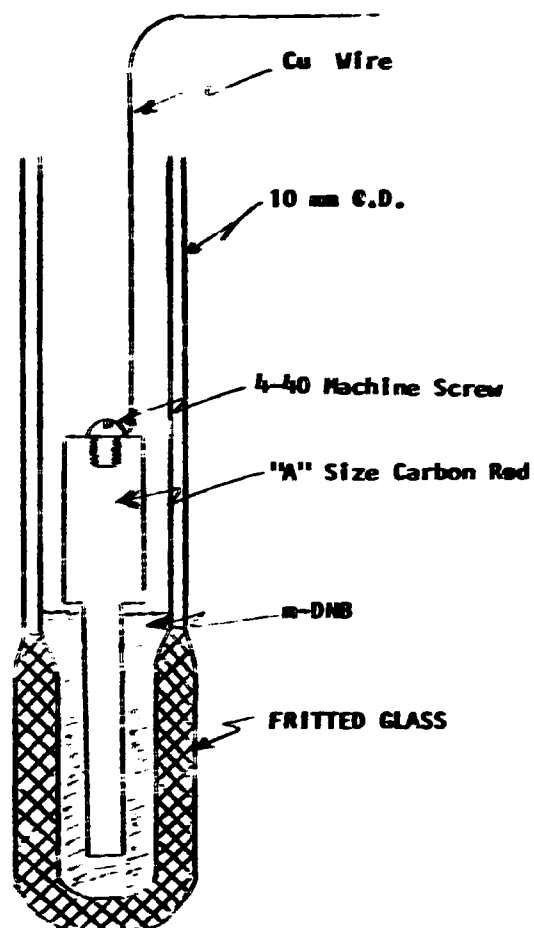
Again, the test electrodes investigated were standard "A" magnesium (AZ-21) cans. A constant surface area was obtained by immersing the open end of each battery can into molten prepurified paraffin wax. As masked, the wax free end of the magnesium can provide a surface area of 14 cm^2 .

The unmasked end of the magnesium can was immersed into the solution being investigated. The electrode remained at open circuit until a stable rest potential was recorded. The can was then initiated by setting the potential of the magnesium test electrode at the initial value for a duration of 10 minutes. Potential increments of 25 mV were used. At the end of 5 minutes the current was recorded.

The electrochemical reduction of meta-dinitrobenzene in the aqueous perchlorate electrolyte has also been initiated. The test electrode arrangement is shown in Figure 1.

The meta-dinitrobenzene was placed in the 10 mm fritted glass bubbler. A standard "A" size carbon rod, machined to 0.110 inch for the bottom 1.0 inch was used as the cathode. This cathode was attached to a Cu lead with a 4-40 machine screw threaded in the top of the carbon rod. This carbon rod assembly was inserted into the inside of the fritted glass bubbler, in which the meta-dinitrobenzene had been placed, with a plunger. This whole assembly was now immersed in the electrolyte. Sufficient time was allowed for diffusion of electrolyte into the bubbler. The rest potential was allowed to

FIGURE 1 CATHODE ASSEMBLY

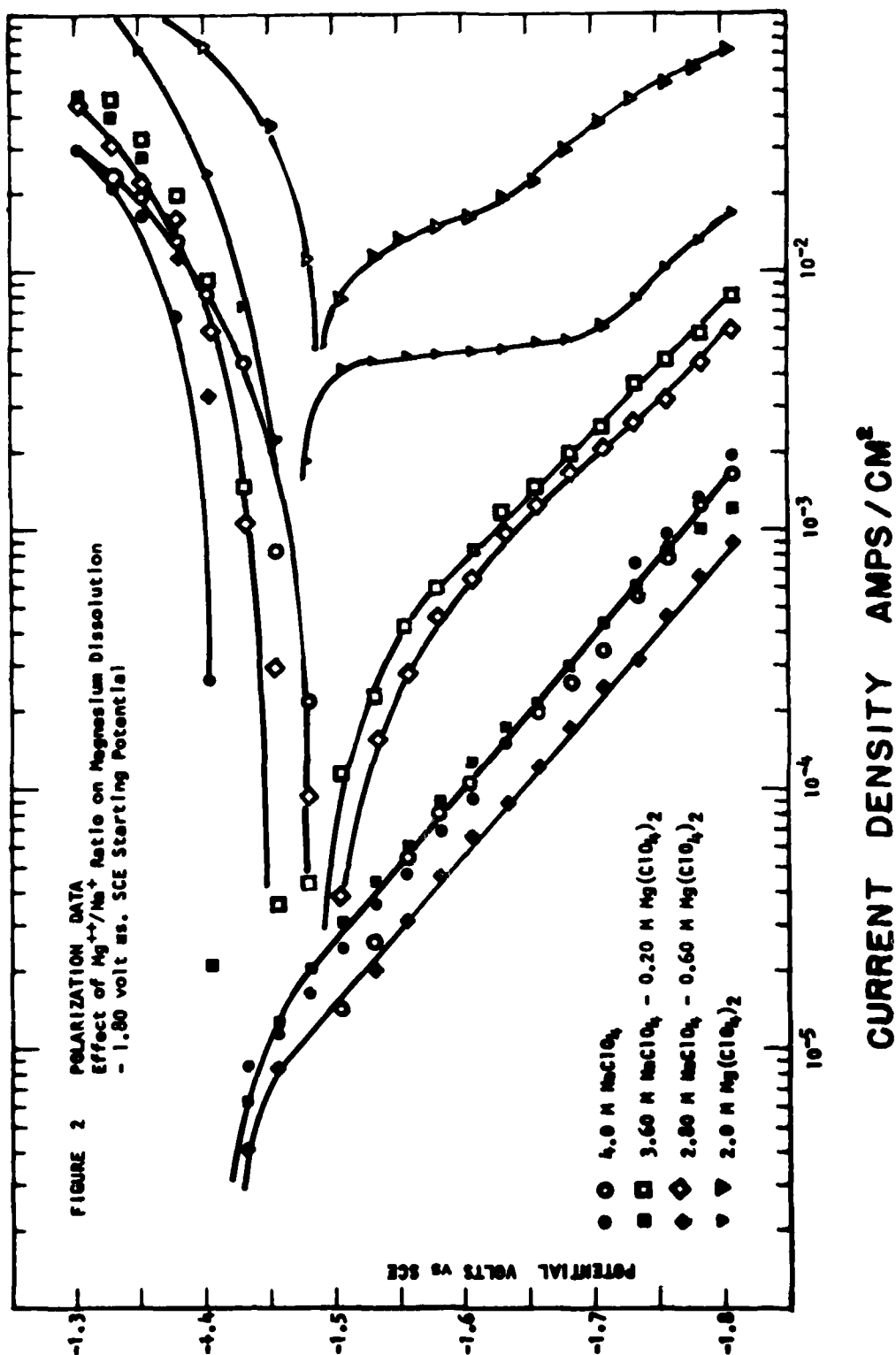


stabilize and was then recorded. The taking of the polarization data was then initiated. The following regime was followed:

1. The chosen potential was applied. The current was monitored on the type 564 Memoscope. When a steady-state current was reached, probably not a true steady-state, the current was recorded. Time duration was approximately 3 minutes.
2. The potential was switched back to the rest potential. The current was monitored until no measurable current passed.
3. The potential was switched to the next chosen value - and so on.

Results and Discussion

Figure 2 shows the polarization data for magnesium (AZ-21) in aqueous perchlorate electrolyte. These data were taken with a starting potential of -1.80v vs SCE. The closed symbols represent data taken with anodic potential steps and the open symbols represent data taken with cathodic potential steps. From Figure 2 it is seen that as the proportion of $\text{Mg}(\text{ClO}_4)_2$ in the electrolyte is increased, the hysteresis between the polarization data taken in the anodic and cathodic direction increased. The corrosion current density also increased sharply. With increasing $\text{Mg}(\text{ClO}_4)_2$ concentration in the electrolyte the magnesium electrode established two, very different, corrosion current densities. These corrosion current densities are,



as Figure 2 shows, a function of the polarization history of the individual electrode and $\text{Mg}(\text{ClO}_4)_2$ concentration. Figure 3 shows similar polarization data for magnesium in aqueous perchlorate electrolyte with a starting potential -1.70v vs SCE. These data exhibit the same characteristic as the data with a starting potential of -1.80v vs SCE. From these figures, it is seen that there is a need for polarization data taken in a solution with the composition

1.60M NaClO_4

1.20M $\text{Mg}(\text{ClO}_4)_2$

and/or

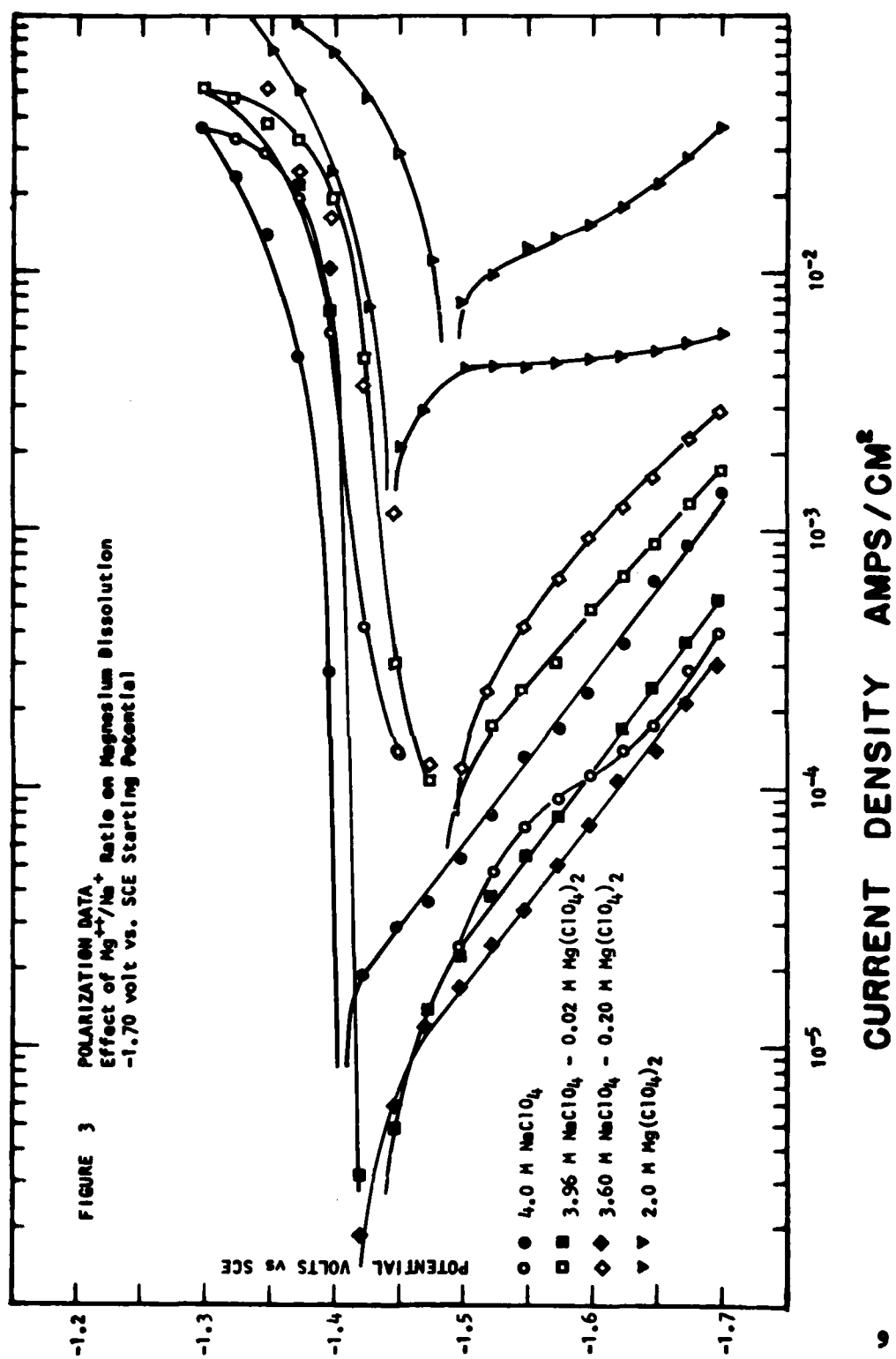
0.80M NaClO_4

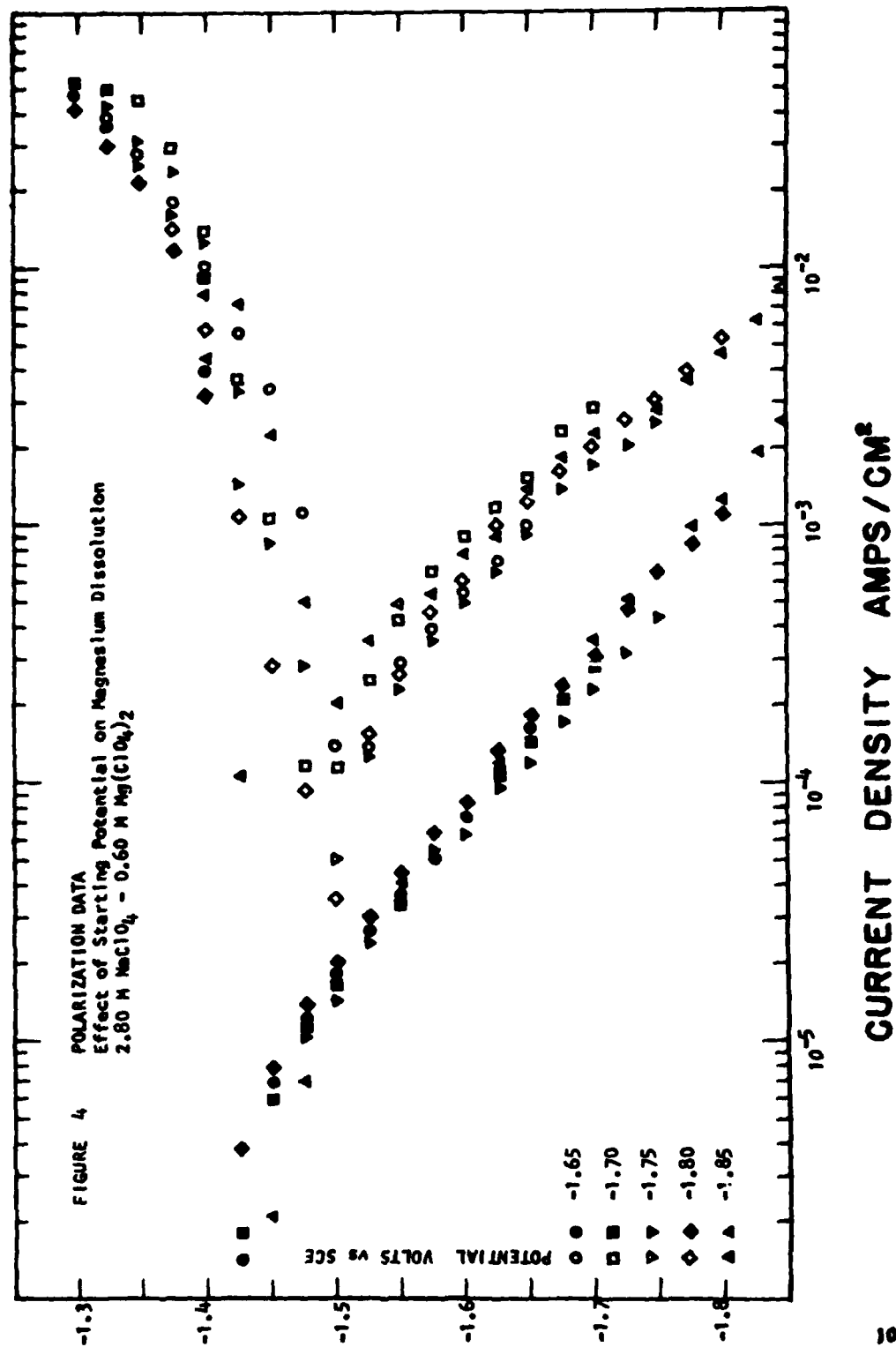
1.60M $\text{Mg}(\text{ClO}_4)_2$

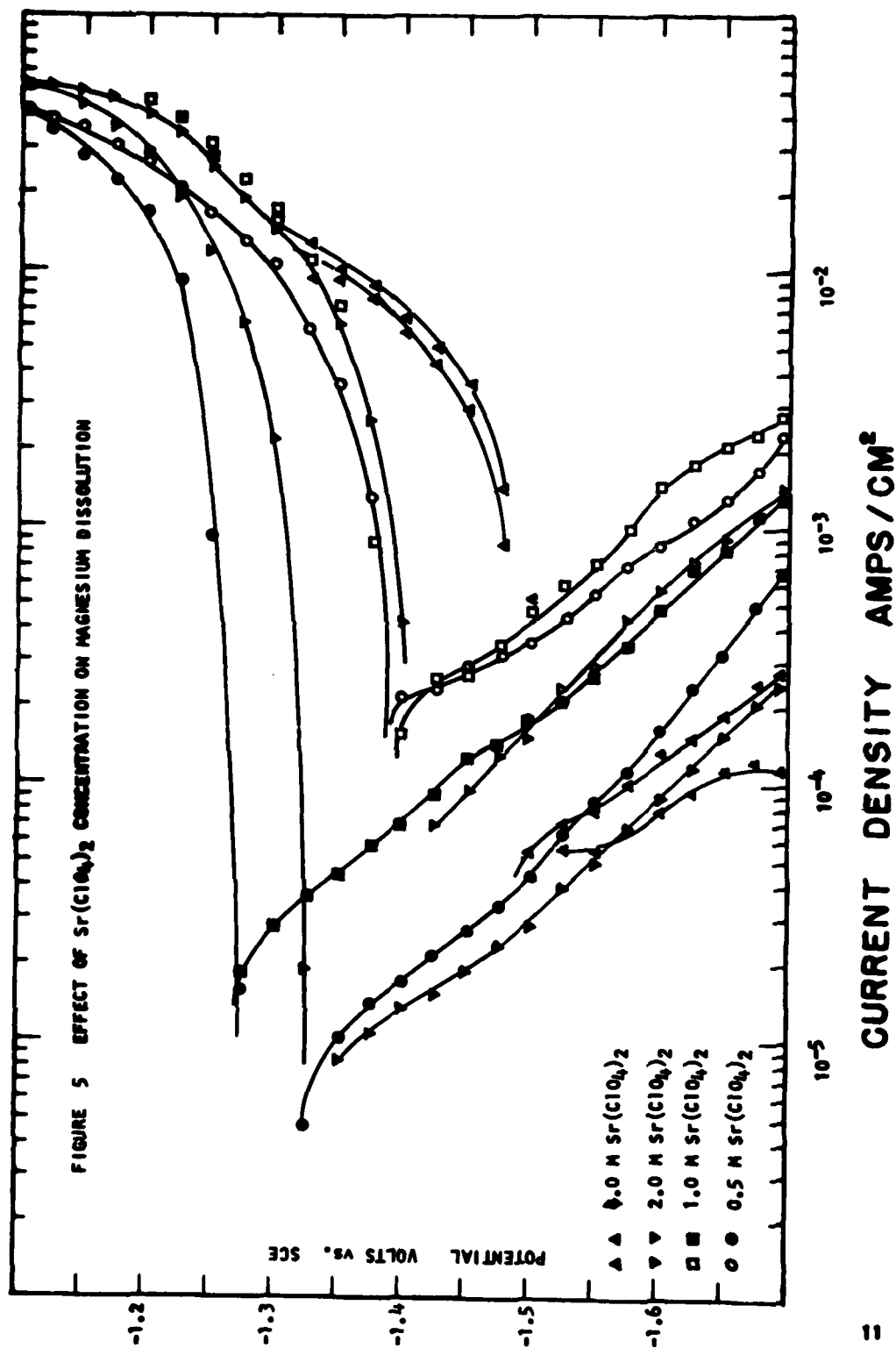
or possibly a greater proportion of $\text{Mg}(\text{ClO}_4)_2$.

Figure 4 shows the effect of starting potential with the electrolyte $2.8\text{M NaClO}_4 - 0.6\text{M Mg}(\text{ClO}_4)_2$. These data are remarkably reproducible for a magnesium electrode. This figure also shows that these data are well behaved and predictable. The starting potential does not appear to influence these data.

Figure 5 shows the polarization data for a magnesium (AZ-21) electrode in $\text{Sr}(\text{ClO}_4)_2$. Concentrations of 4.0M, 2.0M, 1.0M and 0.5M were investigated. The 4.0M $\text{Sr}(\text{ClO}_4)_2$ solution was exceedingly viscous. The polarization data indicate that the rest potential and corrosion current densities are a strong function of concentration. In a given $\text{Sr}(\text{ClO}_4)_2$ electrolyte the magnesium electrode exhibited two apparently

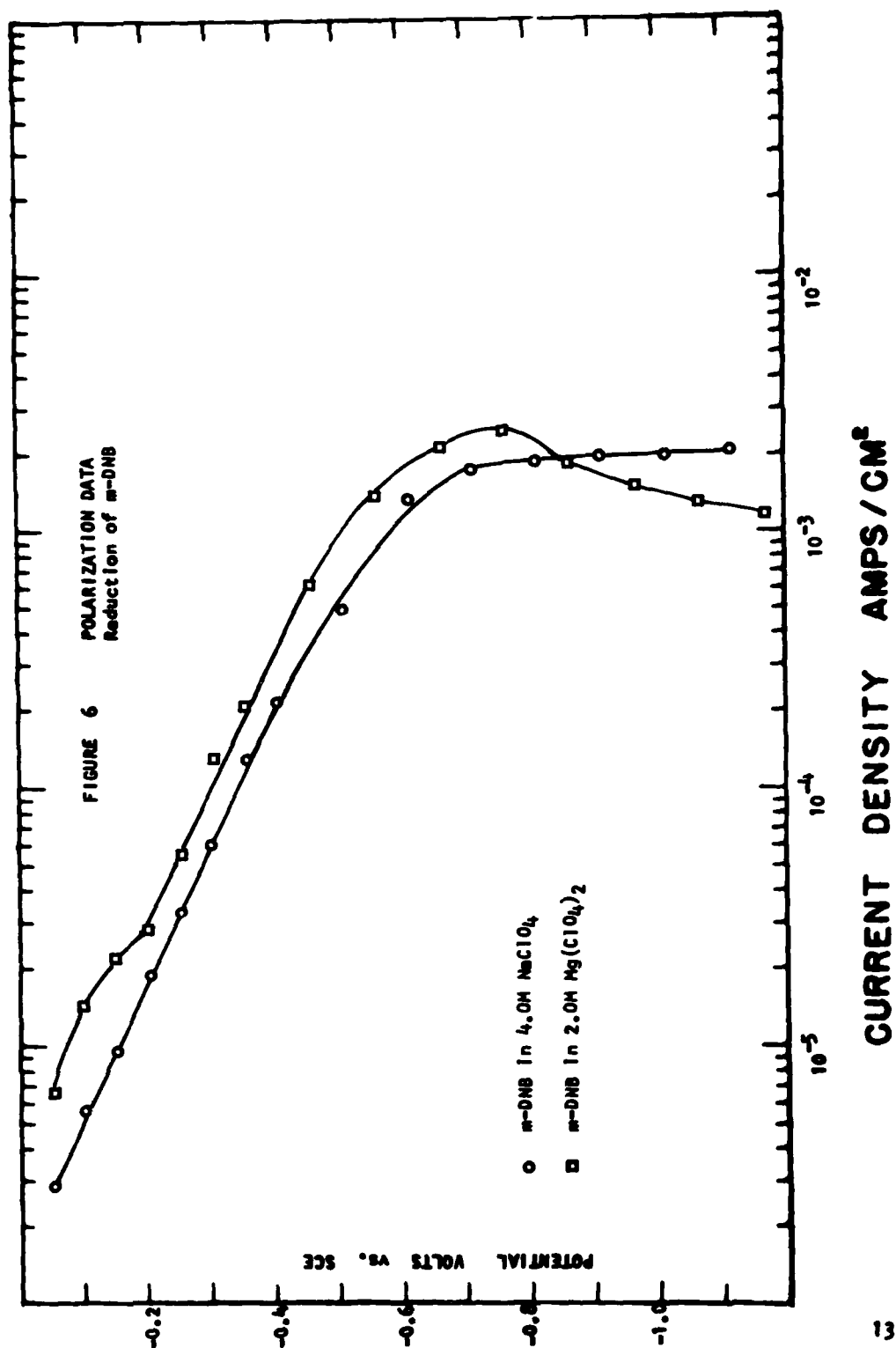






stable corrosion current densities. This phenomena was also observed with $\text{Mg}(\text{ClO}_4)_2$ electrolytes. From Figure 5 it is seen that the $\text{Sr}(\text{ClO}_4)_2$ electrolyte would be a relatively poor choice for a magnesium anode battery. The corrosion current density of the magnesium is relatively large and the polarization at reasonable current densities is excessive.

Figure 6 shows the polarization data for the electrochemical reduction of meta-dinitrobenzene in 4M NaClO_4 and 2M $\text{Mg}(\text{ClO}_4)_2$. The polarization curves appear quite similar, but the reaction products appeared to be quite different. In the NaClO_4 electrolyte the reaction product was blue in color whereas the reaction product in the $\text{Mg}(\text{ClO}_4)_2$ was orange in color. At present an analysis of the product is not available.



Conclusion

1. NaClO_4 appears to be a better electrolyte than $\text{Mg}(\text{ClO}_4)_2$ for the Mg-mDNB cell.
2. $\text{Sr}(\text{ClO}_4)_2$ is an unsatisfactory electrolyte for the Mg-mDNB cell.
3. The rate of reduction of mDNB in NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$ is about equal.
4. The reduction of mDNB appears to yield different reaction products in NaClO_4 and $\text{Mg}(\text{ClO}_4)_2$.

Recommendations for Future Research

1. Further investigation of the dissolution of magnesium and hydrogen evolution reaction on magnesium in the NaClO_4 - $\text{Mg}(\text{ClO}_4)_2$ electrolyte system.
2. Further investigation of the electrochemical reduction of meta-dinitrobenzene in NaClO_4 - $\text{Mg}(\text{ClO}_4)_2$ electrolyte system.
3. Fabrication of "A" size magnesium - meta-dinitrobenzene cells with 4N NaClO_4 electrolyte.
4. Investigation of the dissolution of magnesium, hydrogen evolution reaction on magnesium, and reduction of meta-dinitrobenzene in LiClO_4 - $\text{Mg}(\text{ClO}_4)_2$ and KClO_4 - $\text{Mg}(\text{ClO}_4)_2$ electrolyte systems.

References

1. L. Wikstrom, "Electrode-Electrolyte Interactions:
Magnesium Anode - meta-Dinitrobenzene Cathode", First
Semi-Annual Report, ECCM-0113-1, October, 1968.
2. L. Wikstrom, et al., "Electrode-Electrolyte Interactions:
Magnesium Anode - meta-Dinitrobenzene Cathode", Second
Semi-Annual Report, ECCM-0113-2, August, 1969.

Identification of Key Personnel

Leonard Lee Wikstrom, Assistant Professor - 1/4 time

Akim Adubifa, Graduate Research Assistant - 1/2 time

Gerald Smaldone, Research Technician - 1/4 time

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION
New York University, School of Engineering & Science University Heights Bronx, New York 10453		Unclassified
3. REPORT TITLE		2b. GROUP
ELECTRODE-ELECTROLYTE INTERACTIONS MAGNESIUM ANODES::meta-DINITROBENZENE CATHODES		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Semi-Annual 1 Jan 69 to 30 June 69		
5. AUTHOR(S) (First name, middle initial, last name)		
Wikstrom, J.; A. Adubifa; G. Smaldone; G. Stern		
6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
April 1970		
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S)	
DAAB07-68-C-0143		
a. PROJECT NO. 170 61102 A 34A		
c. Task No. -02	9b. OTHER REPORT NO(S) (Any other number that may be assigned this report)	
d. Subtask No. -32	ECOM - 0143-3	
10. DISTRIBUTION STATEMENT		
This document is subject to special export controls and each transmittal to foreign Governments or foreign nationals may be made only with prior approval of CG, US Army Electronics Command, Fort Monmouth, N.J. ATTN: AMSEL-KL-PF		
11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY	
	Commanding General US Army Electronics Command Fort Monmouth, N.J. ATTN: AMSEL-KL-PF	
13. ABSTRACT		
<p>The electrochemical dissolution of magnesium (AZ-21) and hydrogen evolution reaction on magnesium in $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, $NaClO_4$ and $NaClO_4-Mg(ClO_4)_2$ electrolyte mix have been investigated. The electrochemical reduction of meta-dinitrobenzene in $NaClO_4$ and $Mg(ClO_4)_2$ has also been studied. Polarization data indicate the corrosion current density of the magnesium electrode is much smaller in the $NaClO_4$ than in the other electrolytes studied. In the $NaClO_4 - Mg(ClO_4)_2$ electrolyte mix the corrosion current density of the magnesium electrode increases as the proportion of $Mg(ClO_4)_2$ is increased. In the mixed electrolyte system the magnesium electrode can exhibit two distinctly different corrosion current densities. These corrosion current densities are dependent upon the history of the electrode.</p> <p>The rate of meta-dinitrobenzene reduction in $NaClO_4$ and $Mg(ClO_4)_2$ was found to be about equal. Even though the reduction rate in the two electrolytes was equal, different reaction products apparently were formed.</p>		

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified

Security Classification

5. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High-Energy Battery Systems						
Organic Cathode Materials						
Dinitrobenzene						
Electroreduction						
Magnesium Anodes						
Electrolyte						
Magnesium Dissolution						